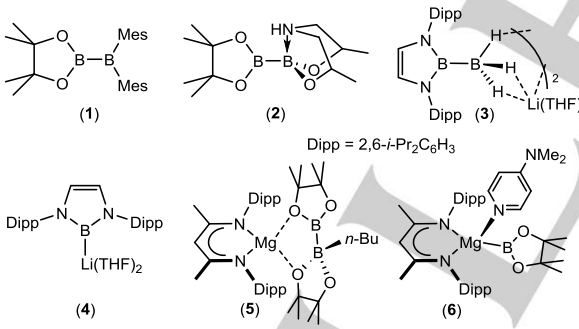
COMMUNICATION

Unsymmetrical Diborane Synthesis by Diborane Metathesis

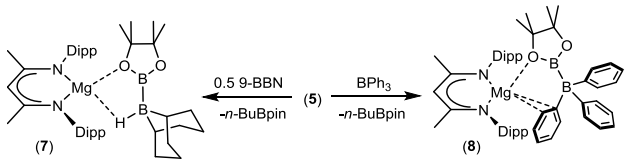
Anne-Frédérique Pécharman,[a] Michael S. Hill,*[a] and Mary F. Mahon[a]

Abstract: Reactions of readily accessible magnesium-centered pinacolatoboryl nucleophiles with $[(Ph_2B)_2O]$ result in B-O bond activation of the diphenylborinic anhydride. Although $[pinBBPh_2]$ is apparently generated when the nucleophilic boron unit is derived *in situ* from a magnesium diboronate, it cannot be isolated due to its onward derivatization by a further $\{Bpin\}^-$ equivalent. A reaction with a terminal magnesium boryl similarly provides a boryloxide by-product. In this case, however, the unsymmetrical sp^2-sp^3 diborane may be intercepted as its DMAP adduct.

The ubiquity of diboranes as reagents in organic chemistry[1,2] has stimulated a growing interest in the rational construction of B-B single bonds.[3] Although a range of alternative routes, including borane dehydrocoupling[4] and metal-centered borylene coupling[5] have been devised, alkali metal reduction of a haloborane persists as the most common means to achieve the synthesis of diborane(4) starting materials such as $[(Me_2N)_2BB(NMe_2)_2]$.[6] This latter classical method, however, is unsuitable for the synthesis of unsymmetrical [B(sp^2)-B(sp^2) or B(sp^2)-B(sp^3)] diboron compounds, e.g. **1** and **2**,[7,8] despite the increasing importance of such compounds as diboration reagents which deliver differentiated boron centers.[1] The realisation of all compounds of this type thus far, has been dependent upon the selective substitution of a single boron center within a reagent containing a pre-existing and symmetrical B-B bond such as bis(pinacolato)diboron (B_2pin_2).[1]



Similar limitations are imposed by the Wurtz-type C-C coupling of alkyl halides in organic synthesis and it is clear that the development of B-B bond forming protocols more closely comparable to nucleophilic (e.g. S_N2) C-C coupling would enable a much greater diversity of diborane structure. In this latter regard, however, a severe restriction to progress is imposed by the relative dearth of conveniently accessed and structurally desirable boron nucleophiles.[9] In the context of B-B bond formation, Yamashita and Nozaki have described the lithium boryltrihydroborate (**3**)[10] and a triborane(5) derivative,[11] which were synthesized by reaction of the nucleophilic lithium boryl anion (**4**)[12] with the boron electrophiles, BH_3·THF and BF_3·OEt_2, respectively. The isolation of the boron nucleophile (**4**) itself, however, requires strongly reducing reaction conditions and is dependent on the kinetic stabilisation provided by bulky substituents, which is undesirable for onward applications in synthesis. With these limitations in mind, we have recently shown that treatment of the readily prepared diboronate derivative **5** with 4-dimethylaminopyridine (DMAP) yields the magnesium derivative **6**, comprising a nucleophilic terminal $\{Bpin\}^-$ anion.[13] Subsequently, we have reported that compound **5** itself reacts as a source of the $\{Bpin\}^-$ nucleophile when treated with the electrophilic borane reagents, BPh_3 and 9-borabicyclo[3.3.1]nonane (9-BBN) and enables facile B-B formation (Scheme 1).[14] The resultant diborane(5) anions of compounds **7** and **8**, however, were found to be stable to the requisite B-Ph and B-H elimination processes and liberation of the neutral unsymmetrical diborane(4) molecules could not be achieved. In this contribution, we extend our study of compounds **5** and **6** to their reactivity with diphenylborinic anhydride, $[(Ph_2B)_2O]$,[15] an easily accessible synthon for electrophilic $\{Ph_2B\}^+$ furnished with a labile $\{Ph_2BO\}^-$ leaving group. The resultant reactivity provides a practicable means to achieve B-B bond formation and the generation of unsymmetrical diboranes.



Scheme 1: Synthesis of the stable magnesium diborane(5) derivatives, **7** and **8**.

An initial reaction performed between equimolar quantities of compound **5** and $[(Ph_2B)_2O]$ was monitored by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy. Although the synthesis was observed to provide two new β-diketiminate derivatives, compounds **9** and **10**, in approximately equal quantities along with the anticipated production of *n*-BuBpin [δ (^{11}B) = 34.2 ppm] at room temperature, this process ensued with only 50% consumption of the diphenylborinic anhydride reagent. Repetition of the reaction with only 0.5 relative equivalents of $[(Ph_2B)_2O]$ provided similar conversion to the new species **9** and **10** but resulted in complete consumption of the anhydride reagent. The solvent was removed from this reaction after 20 hours at room temperature and washed with hexane. Crystallization of the resultant solid from a saturated toluene solution provided colorless single crystals of compound **9** while crystallization from the hexane washings yielded crystals of

[a] Dr. Anne-Frédérique Pécharman, Prof. Michael S. Hill, Dr. Mary F. Mahon
Department of Chemistry
University of Bath
Bath, BA2 7AY, UK.
E-mail: msh27@bath.ac.uk

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compound **10**, both of which were analyzed by single crystal X-ray diffraction. The resultant experiments revealed compound **9** to be a magnesium derivative of a triborane(6) anion, in which the B-B-B skeleton is propagated by a central {BPh_2} unit and two flanking {Bpin} moieties (Figure 1a), and compound **10** as a magnesium complex of a terminal {$OBPh_2$}$^-$ anion. In this latter compound the remaining coordination site of the β-diketiminato magnesium center is occupied by a molecule of *n*-BuBpin, which binds through coordination of one of the pinacolato oxygen atoms (Figure 1b).

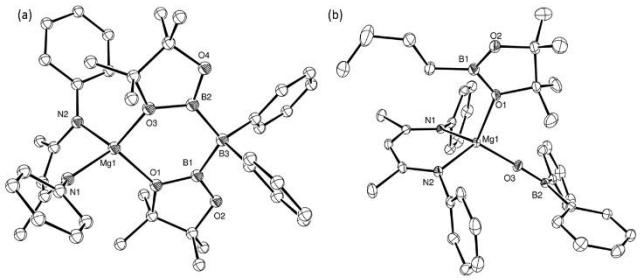
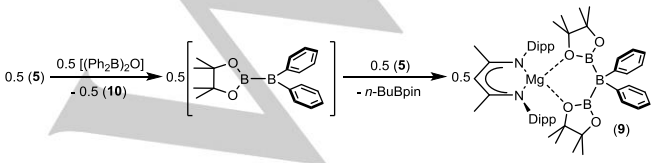


Figure 1: ORTEP representations (30% probability ellipsoids) of (a) compound **9** and (b) compound **10**. Hydrogen atoms and *iso*-propyl carbon atoms are removed for clarity in addition to the disorder in **10**. Selected bond length (Å) and angles (°): (**9**) Mg1-O1 2.0698(13), Mg1-O3 2.0097(13), Mg1-N1 2.0565(15), Mg1-N2 2.0593(16), B1-B3 1.717(3), B2-B3 1.710(3), O3-Mg1-O1 101.97(5), O3-Mg1-N1 118.50(6), O3-Mg1-N2 113.88(6), N1-Mg1-O1 112.68(6), N1-Mg1-N2 93.59(6), N2-Mg1-O1 117.14(6), B2-B3-B1 115.29(16); (**10**) Mg1-O1 2.1243(17), Mg1-O3 1.8492(16), Mg1-N1 2.0496(18), Mg1-N2 2.0616(18), O3-B2 1.317(3), O3-Mg1-O1 104.00(7), O3-Mg1-N1 118.29(7), O3-Mg1-N2 117.82(8), N1-Mg1-O1 111.44(7), N1-Mg1-N2 94.64(7), N2-Mg1-O1 110.75(7).

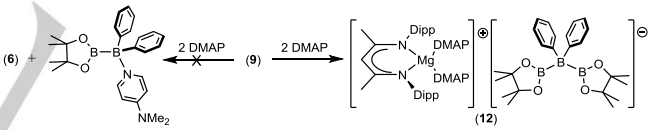
The catenated B-B-B chain of the boron-containing anion in compound **9** is reminiscent of the triborane(6) unit of [HC{(Me)CN(Dipp)}$_2$Mg{B_3pin_3}] (**11**), which we have previously reported to result from treatment of compound **5** with a further equivalent of B_2pin_2.[13] In both compounds **9** and **11** the triboron skeleta of the anions are propagated via sequences of electron precise (2c-2e) bonds. Although the anionic B(sp^2)-B(sp^3)-B(sp^2) structures of both derivatives appear to be unique to these compounds, the individual B-B bond lengths of both **9** and **11** lie within the ranges [ca. 1.70 – 1.74 Å] established for various neutral triborane molecules in which the catenate propagates wholly through trigonal boron centres.[16-19] Boryloxide ligands bearing more sterically demanding aryl substitution are relatively common and, indeed, three examples of dimagnesium derivatives with {Mg-(μ_2-$OBMes_2$)-Mg} bridging interactions have been structurally elucidated.[20] Compound **10** is, however, unique in comprising a terminal diphenyl boryloxide unit, while its *n*-BuBpin ligand appears to provide the sole example of such a metal-coordinated neutral organoboronic ester.



Scheme 2: Synthesis of compounds **9** and **10**.

The definitive identification of compounds **9** and **10** accounts for the observed 1:0.5 reaction stoichiometry between compound **5** and [$(Ph_2B)_2O$]. Although other pathways may be in operation, these and subsequent (*vide supra*) observations allow the reactivity to be rationalized as shown in Scheme 2. As we have previously observed,[14] compound **5** reacts as a source of the {Bpin} nucleophile, in this case to attack a boron center of the borinic anhydride. The displaced boryloxide component and the resultant equivalent of *n*-BuBpin are retained within the magnesium coordination sphere of compound **10**, while the resultant but unobserved unsymmetrical diborane, [pinBBPh_2], reacts immediately with a further half equivalent of compound **5**. This process takes place with the displacement of *n*-BuBpin and generates compound **9** by reaction of the incipient {Bpin} nucleophile at the more electrophilic {BPh_2} center of the unsymmetrical diborane.

This proposed route to compound **9** can be considered as effectively analogous to that observed for the reaction of **5** with a further equivalent of [B_2pin_2] to generate compound **11**.[13] Reaction of this latter species with DMAP was also previously observed to generate the terminal boryl derivative (**6**) through displacement of [B_2pin_2].[13] In an attempt to induce a similar generation of **5** through the elimination of the unsymmetrical [B(sp^2)-B(sp^3)] diborane [pinBBPh_2(DMAP)], compound **9** was reacted with two molar equivalents of DMAP (Scheme 3). This procedure, however, resulted in the rapid crystallization of a further new compound (**12**), which was identified by a single crystal X-ray diffraction analysis (Figure 2) as the charge separated ion pair complex, [HC{(Me)CN(Dipp)}$_2$Mg(DMAP)$_2$]$^+$ [pimBBPh_2Bpin]$^-$, in which the triborane(6) anion maintains its integrity as a non-coordinated entity (Scheme 3).



Scheme 3: Reaction of compound **9** with two molar equivalents of DMAP to provide the ionic compound **12**.

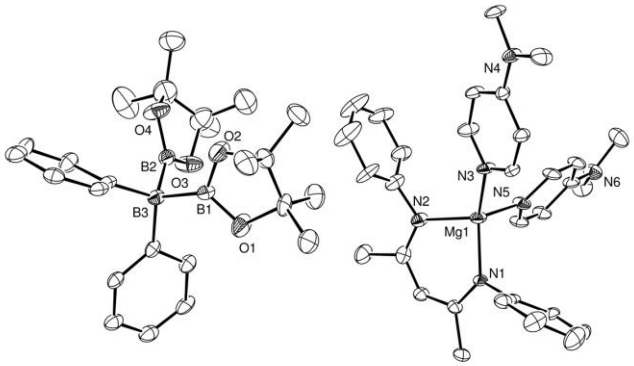
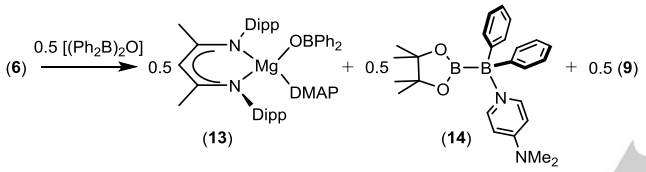


Figure 2: ORTEP representation (30% probability ellipsoids) of the Mg1-containing cation and the B1-containing anion of compound **12**. Hydrogen atoms, *iso*-propyl carbon atoms and the anion disorder are removed for clarity. Selected bond length (Å) and angles (°): N1-Mg1 2.015(3), N2-Mg1 2.011(4), N3-Mg1 2.075(4), N5-Mg1 2.049(4), B1-B3 1.700(7), B3-B2 1.675(7), B2-B3-B1 101.2(4).

Reactions of the terminal magnesium boryl, compound **6**, were also performed with $[(Ph_2B)_2O]$ in a relative 1:0.5 stoichiometry. Monitoring of these reactions by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy was again indicative of the generation of compound **9**, which was formed in an effective equimolar quantity with a single new β-diketiminato magnesium derivative (**13**). This latter species displayed distinctive unresolved multiplet resonances in its ^1H NMR spectra at δ 5.56 and 8.00 ppm, which were consistent with the presence of a magnesium-coordinated DMAP ligand. Notably, additional well resolved doublet signals of a similar intensity were also observed in these spectra at δ 5.52 and 8.15 ppm, indicative of the presence of a further DMAP-coordinated reaction product (**14**). Although the corresponding $^{11}B\{^1H\}$ NMR spectra were broad and uninformative, the origin of these observations was resolved by fractional crystallization and the isolation of pure samples of compounds **13** and **14** from the reaction solution. A single crystal X-ray diffraction analysis revealed compound **13** to be an analogue of the terminal boryloxide derivative **10** in which the coordinated *n*-BuBpin has been replaced by a molecule of DMAP (Figure 3a). A further X-ray analysis identified compound **14** as the neutral sp^2-sp^3 diborane, [pinBBPh$_2$(DMAP)], and allowed the overall course of the reaction to be rationalized as shown in Scheme 4.



Scheme 4: Reaction of compound **6** with $[(Ph_2B)_2O]$.

Although the structure of compound **14** is in itself unremarkable, it provides the first example of an unsymmetrical diborane to be prepared by an effective nucleophilic displacement of a boron-bound leaving group by a boron-centered nucleophile. We suggest that this unique observation holds rich potential for further elaboration that will enable much greater structural diversity for this increasingly important class of molecule.

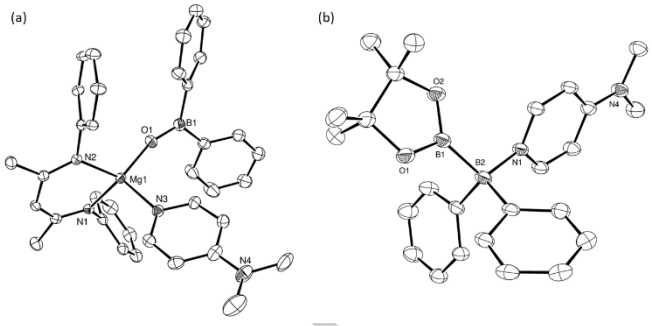


Figure 3: ORTEP representations (30% probability ellipsoids) of (a) compound **13** and (b) compound **14.** Hydrogen atoms and, in compound **14**, *iso*-propyl carbon atoms are removed for clarity. Selected bond length (Å) and angles (°): (**13**) Mg1-N3 2.117(3), Mg1-O1 1.856(3), Mg1-N1 2.053(3), Mg1-N2 2.037(3), O1-B1 1.310(5), O1-Mg1-N1 125.97(12), O1-Mg1-N2 113.53(12), O1-Mg1-N3 100.85(12), N1-Mg1-N3 112.05(11), N2-Mg1-N1 92.56(11), N2-Mg1-N3 112.21(11), B1-O1-Mg1 161.9(3); (**14**) B1-B2 1.730(4), O1-B1 1.381(4), O2-B1 1.385(4), N1-B2 1.625(4), N1-B2-B1 110.6(2).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: magnesium • boryl • borane • diborane • main group chemistry

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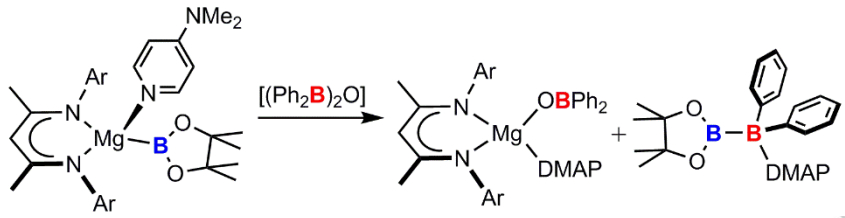

Anne-Frédérique Pécharman, Michael S. Hill, Claire L. McMullin* and Mary F. Mahon*

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Unsymmetrical Diborane Synthesis by Diborane Metathesis

Getting from B to B: Reactions of a magnesium-based pinacolatoboryl nucleophile with $[(Ph_2B)_2O]$ provide facile B-O metathesis and allow the isolation of the unsymmetrical diborane.